

# Pb induces superconductivity in $\text{Bi}_2\text{Se}_3$ analyzed by point contact spectroscopy

P. Arevalo-López, R. E. López-Romero, and R. Escudero(1)

*Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México. A. Postal 70-360. México, D.F., 04510 MÉXICO.*

(Dated: December 31, 2015)

Some topological insulators become superconducting when doped with Cu and Pd. Superconductivity in a non-superconductor may be induced by proximity effect: i.e. Contacting a non-superconductor with a superconductor. The superconducting macroscopic wave function will induce electronic pairing into the normal compound. In the simplest topological insulator,  $\text{Bi}_2\text{Se}_3$ , superconductivity may be induced with Pb. We studied with point contact junctions formed by contacting  $\text{Bi}_2\text{Se}_3$  crystals and Pb, glued and pressed with silver paste and/or applying low heat to the Pb to improve the contact. Junctions were formed with a thin tungsten plated gold W(Au) wire as one electrode, and the other  $\text{Bi}_2\text{Se}_3$  and Pb. We study the characteristics of the electron coupling; the transition temperature,  $T_C$ , evolution with temperature of the energy gap,  $\Delta$ , and  $2\Delta/K_B T_C$  ratio. The superconductor  $\text{Bi}_2\text{Se}_3$ -Pb behaves different as explained in the classical BCS theory. In BCS a superconductor is only weak or strong coupled, depending on the electronic interaction that form the electronic condensate. This differentiation is given by the size of the mentioned ratio. BCS Typical values are 3.53 to about 4.3 for weak or strong coupling limits respectively. In this study performed in  $\text{Bi}_2\text{Se}_3$ -Pb we found different values to the normal ones from 10 to 23, indicating very strong limit. Those values never have been observed in other superconductor. The transition temperatures found varies from 2.7 to 7 K. This information and other results will be presented in this paper.

## I. INTRODUCTION

With the discovery of topological insulators (TI) [1–3] many theoretical and experimental studies have been made in order to improve our knowledge of its new properties. In this work we are interested in the superconducting behavior induced by the so called proximity effect studied with point contact junctions (PCS), and in the new properties of these TI superconductors [4–10]. In the new TI;  $\text{Bi}_2\text{Se}_3$  and  $\text{Bi}_2\text{Te}_3$  was found that both compounds become superconducting when copper or palladium are doped or intercalated in the structural gaps between TI layers [6–8, 10–15]. In these superconductors the transition temperatures are low,  $T_C \sim 3 - 5.5$  K [6–8, 10]. Actually many work with TI are been performed to determine other metals that can produce superconductivity. The interest in these new superconductors is to found the general behavior and to understand if they present similar electronic pairing mechanism as given by the BCS theory [8–10]. In BCS the electron pairing is due to the interaction between two electrons at the Fermi surface by a phonon exchanged of the lattice structure. Among the important parameters and variables of the theory, one is very related to the pair formation, the  $2\Delta/K_B T_C$  ratio, where  $\Delta$  is the energy gap,  $T_C$  is the transition temperature, and  $K_B$  the Boltzmann constant. In BCS theory two possibilities exist for the strength of the pair formation, the weak or strong coupling limit. The weak limit is given by the number 3.53, whereas for the strong limit the value is slightly above the weak. For instance Pb, a typical strong coupled superconductor the coupling is 4.3. Many more values for the ratio can be found in Table 5.2 in Poole book for conventional superconductors [16]. In unconventional superconductor the

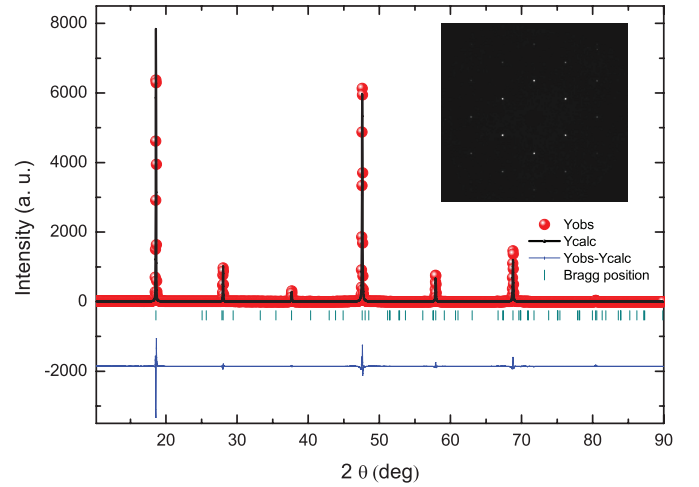


FIG. 1: (Color online) X- ray diffraction data of the  $\text{Bi}_2\text{Se}_3$  single crystal, and Rietveld refinement. Only the  $(00l)$  reflections are observed. Inset shows electron diffraction data of a thin layer of the crystal.

behavior may be very different, but no so, as Cuprates, Arsenides, Fe based, etc. In these compounds the ratio varies from 7 to about 8, although some of those values may be controversial as estipulate in different publications. However this ratio has ever found bigger than 10 [17–22]. The conventional wisdom related to big values of the mentioned ratio is that superconductors with different type of electron pairing could have different BCS microscopic mechanism.

One of the main reasons to study superconductivity in TI induced by proximity effect in  $\text{Bi}_2\text{Se}_3$  is that it is the simplest one found at present, with simple Dirac

cone and large band gap, it has a very simple surface states, which is quite different to  $\text{Bi}_2\text{Te}_3$ , the other well known TI. This last TI has a large deviation of the Dirac cone and this deviation can introduce extra difficulties to understand the induced superconductivity. Hasan has pointed out that in this TI may be induced a two dimensional superconductor state [3], in similar form as occurs in the high  $T_C$  superconductors. i.e., this implies that the majorana states may be manipulated [23] and including the possibility to observe features and effects related to those modes, and as final result different superconducting mechanisms related to different electronic coupling. This assumption was discussed by Qi and Zhang supposing that in this TI could be induced a non trivial topological superconductor and perhaps to be one of the ways to probe the existence of majorana modes [4].

For the study of the induced superconductivity in  $\text{Bi}_2\text{Se}_3$  we choose PCS junctions as the experimental tool. Tunneling and point contact spectroscopies are simple tools and well appropriate to study superconductivity. The compound was prepared with  $\text{Bi}_2\text{Se}_3$  contacted with Pb. A Pb foil induce the proximity effect because the macroscopic wave function of the superconducting state produces the pair formation inside the TI when two materials are in very close proximity. Our study was performed using point contact junctions (PCS). These junctions could give information about the microscopic mechanisms for the pair formation, and features and structure of the Andreev reflections, and information about the energy gap.

Before to start the study, it is important to determine the working regime of our PCS junctions. From theoretical bases we determined the junctions working regime using the BTK, model, which is well known [24]. In this model the microscopic parameter used to determine and characterize the junctions parameters can indicates if it behaves as tunnel or metallic contact.  $Z$  is the parameter used which according to the value, determines the junctions behavior. A small value, close to zero means junctions with pure Andreev behavior thus, a metallic contact. Whereas values above zero mark the transition from metal contact to tunneling regime. Value from above 1.5 may be considered with almost tunneling behavior.

Preparation of the single crystal  $\text{Bi}_2\text{Se}_3$  were produced by mixing stoichiometric amounts of high purity Bi pieces, (Sigma-Aldrich 99.999%), and Se (Alfa Aesar 99.999%), were grounded, pressed into pellets and sealed in evacuated quartz tubes, heated for about 9 h to a maximum temperature of 850 °C and held at this temperature for about 24 h. After this procedure the tube was slowly cooled to 630 °C and annealed for 24 h. The last step was performed by quenching the tube into water at room temperature. The single crystals present a plaquette-like shape, length sizes about 0.5 - 1 cm, and 0.1 to 0.5 width. Phase identification was done with X-ray diffractometer, Bruker D8 in a Bragg - Brentano geometry. Also electron diffraction microscopy was performed. For this study mechanical exfoliation was per-

formed.

Surface morphology was determined in a scanning electron microscope FEG JEOL-7600F equipped with X-ray energy dispersive analyzer Oxford INCA X-Act. Selected-area of electron diffraction patterns were obtained in a Transmission Electron Microscope JEOL JEM-1200EX. The crystal structure was confirmed by X-ray diffraction, Fig. 1, by comparison with X-ray of  $\text{Bi}_2\text{Se}_3$  and Database (ICSD: 04 - 2545). The patterns show a single phases. Reflections are very sharp indicating the high crystallinity and (00 $l$ ) reflections from the basal plane of cleaved sample and absences for the  $R\bar{3}m$  rhombohedral space group.

The structural characteristics of  $\text{Bi}_2\text{Se}_3$  are the following; it has a rhombohedral crystalline structure with space group  $R\bar{3}m$  [25, 26], and parameters as  $a = 4.143$  Å, and  $c = 28.636$  Å. The structure is formed by layers, with three double-layers of sharing-edges  $\text{Bi}_2\text{Se}_6$  octahedra stacked along the [00 $l$ ] direction, equivalent to the  $\text{Se1} - \text{Bi} - \text{Se2} - \text{Bi} - \text{Se1}$  quintuple layers as often referred in the literature [8, 27, 28]. These double-layers are weakly bonded via van der Waals interactions, resulting in an easy cleavage material [27]. According, the structural characteristics  $\text{Bi}_2\text{Se}_3$  may accept many chemical modifications either by substitution or by intercalation between the double-layers. To induce superconductivity by proximity effect we used a thin Pb foil, pressed and/or glued to the TI with silver paint or by mechanical attachment with low heating as well. Similar experiments have been performed using mechanical gluing with different high or low transition temperature superconductors [11, 12, 29–31]. The spectroscopic characteristics determined with PCS junctions, were formed with  $\text{Bi}_2\text{Se}_3$ -Pb (TI-Pb) as the main electrode, and the other one to complete the junction was a thin wire of W(Au) 5  $\mu$ -m diameter. The spectroscopic characteristics, the Andreev reflections, transition temperatures, energy gaps, etc, were observed at low temperature. The number of studied PCS's shown different transition temperatures, depending in the close contact in both materials. The energy gap extracted with the measured differential conductance characteristic,  $dI/dV$ , showed the evolution of the energy gap with temperature. The transition temperature, evolution with temperature of the energy gap, and the  $2\Delta/K_B T_C$  ratio were determined. The ratio gives values quite anomalous and big showing values from 10 to 23. Additionally, extra information was obtained by determining the spectral features of the structure in the derivative of the differential resistance obtained at the lowest temperature. Clearly the structure may be related to the phonon spectra of the two components, the  $\text{Bi}_2\text{Se}_3$  and the Pb. The correlation of effects related to phonon structure were observed and determined in PCS by Yanson many years ago [32].

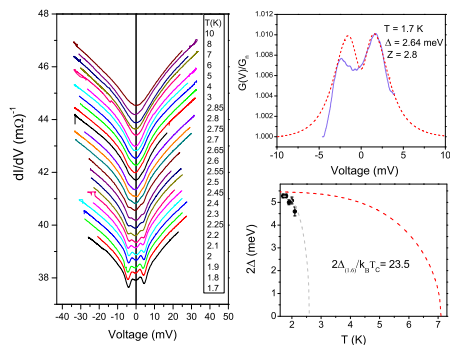


FIG. 2: (Color online) Differential conductance of a  $\text{Bi}_2\text{Se}_3$ -Pb junction from 1.7 to 10 K, left panel. At low temperature are clearly noted the spectral characteristics of the energy gap feature. Above 3 K small features are distinguished related to the superconducting Pb. Top right panel shows BTK fit of  $G(V)/G_n$  - Bias voltage of the energy gap features at  $T = 1.7$  K induced by Pb, parameters were;  $\Delta = 2.64$  meV,  $Z = 2.8$ . The right lower panel shows the evolution of the energy gap with temperature. The red line) is BCS for Pb,  $2\Delta/k_B T_C$  ratio is this junction was 23.5.

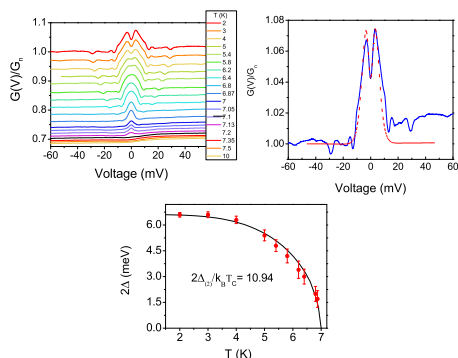


FIG. 3: (Color online) Left panel shows the differential conductance of a PCS junction, the transition temperature was very close to the Pb transition. All curves were vertically displaced by a small amount in order to have a clear view of the spectroscopic features. Right panel shows the fit with BTK model values were  $\Delta = 3.3$  meV, and  $Z = 0.73$  at 2 K. The lower panel shows the temperature evolution of the energy gap. The lower panel also shows the anomalous big  $2\Delta/k_B T_C$  ratio.

## II. RESULTS AND DISCUSSION

The characteristics of the TI cell parameters were determined by Le Bail fitting,  $a = 4.1265(1)$  Å and  $c = 28.6349(2)$  Å. Results related to the structural characterization are in Fig. 1. There we present the X-ray and Rietveld refining. The inset is the spectrum of electron diffraction of a thin layer of the single crystal used in

this experimental work. Data and spectrum show good structural characteristics of the single crystal.

All PCS's junctions studied were formed by a small crystal layers of  $\text{Bi}_2\text{Se}_3$ , the thickness about  $0.1 - 0.35$  mm, and a foil of Pb with similar size of the  $\text{Bi}_2\text{Se}_3$ . The two materials, Pb and TI were pressed together and glued with diluted silver paint, and sometime a low heat was applied to Pb in order to increase the contact. Both materials were pressed with a small press to increase the contact. This simple manner was used to maintain together the two materials and induces the proximity effect in the  $\text{Bi}_2\text{Se}_3$ . As mentioned PCS's were fabricated by using a thin wire of W(Au),  $5 \mu\text{m}$  diameter contacting the TI-Pb sample on the TI surface. Junctions differential resistances varied from 1 to  $25 \Omega$ . Other PCS's with very small differential resistances, in the order to 1 to  $5 \Omega$  were discarded because heating effect distorted the spectral characteristics and were unstable, only high resistance values, about 20 -  $25 \Omega$  were used avoiding heating effects. The number of PCS's fabricated were sufficient to obtain a clear picture and reproducibility. Measured PCS's were more than 30 - 40. Only well reproducible results were taken into account. Differential resistance ( $dV/dI - V$ ) was obtained with the normal tools for tunneling studies; Lock-in amplifier and bridge, the inverse of ( $dV/dI - V$ ),  $G(V)$ , was digitally obtained. As is well known  $G(V)$  at low temperatures is proportional to the density of electronic states, and information about the gap was obtained.

Figures 2 to 4 show result of our measurements performed in three different PCS's. The differential conductance of these PCS's have similar values, but presents different spectroscopic features, which will be related to the coupling of the TI-Pb system. The spectroscopic features of the PCS varies because the closeness contact in both materials. The features are therefore due by the coupling of the superconducting macroscopic wave function into the normal material. This coupling readily may be determined by the transition temperature, size of the energy gap and  $2\Delta/k_B T_C$  ratio, and by the spectroscopic features observed on the background of  $G(V - eV)$  from low energies up to relative high values (similar to occurs with the determination of phonon spectrum in normal superconductors) and low temperature, after the subtraction of the energy gap was performed. Figure 2 is the result of a measured PCS with  $Z = 2.8$  and  $\Delta = 2.64$  meV values at a temperature of 1.7 K. Right panel shows the fitting of the normalized differential conductance ( $G_n$  determined at 1.7 K. In this figure the data is the continuous line whereas the pointed line is the fit to the BTK model.

Fig. 2 right lower panel displays the temperature evolution of the energy gap, two curves are shown; the curve that displays the energy gap at about 2.5 K is the result of the proximity effect in TI-Pb system. We displayed the BCS evolution of the energy gap with temperature of the Pb, for reference to emphasize the similar values of the energy gap in this TI-Pb system. The  $2\Delta/k_B T_C$

ratio is incredible big, about 23.5. This value was the biggest in all our experiments.

Fig. 3 shows another PCS's data measured from 2 to 10 K, left panel. The energy gap features are clearly observed at low temperatures and disappears at about 7.1 - 7.2 K. Above 10 K no structural features are observed. As in the other junctions characteristics at low temperature the gap feature, clearly is seen at the center of the curves, close to zero bias, and decreasing with the increasing temperature. This figure also shows the normalized data measured at 2 K, Panel right shows BTK fitting with  $Z = 0.73$ , and  $\Delta = 3.3$  meV. This PCS behaves as a metallic contact, with spectroscopic features only related to Andreev reflections [32]. More information was obtained from data of the same PCS. Above the energy gap bias voltage the structure in the Differential conductance clearly may be related to phonon spectrum of the TI-Pb system, as explained many years ago by Yanson when studying in point contact junctions [32]. It is interesting to pointing out another characteristics seen in our junctions. Close to the zero bias voltage the features related to the energy gap displayed a non symmetric structure. This can be see in the Data of Fig. 3, in the right panel the two peaks have different values, one bigger to the another. These nonsymmetric peaks are shown in figures 2 and 3. The two conductance peak of the energy gap feature show different conductance values. This anomalous characteristic looks quite similar to the observed and found in heavy superconductor and in other physical systems. For example similar characteristics were found in  $\text{URu}_2\text{Si}_2$  [33]. The anomaly was related to a Fano resonance [34], and here in these experiments the anomaly could be explained as an extra interaction still not considered in the TI.

Lastly in this figure, the lower panel displays the evolution of the energy gap feature with temperature. The transition temperature was 7.1 K, only a little below Pb transition. However, the  $2\Delta/K_B T_C$  ratio, as in previous experiments it is big, 10.94. Here at this point we need to analyze the values and size of the ratios: With lower transition temperatures ratio values are bigger with small transition temperatures, whereas high transition temperatures shows lower ratios.

The last PCS junctions measured are presented in Figs. 4, it shows the overall evolution from 1.8 K to 7.2 K. Close to zero bias voltage are the features of the energy gap. More structure was observed here. Differential conductance curve fitted with BTK at 1.8 K, gave  $Z = 6.8$  which indicate a tunnel junction, with gap,  $\Delta = 3.8$  meV. Again the spectroscopic features of the gap, as in the other case are anomalous, both peaks are different in conductance value. However the energy gap evolution as in other PCS's follows BCS, Here the detrmned ratio was 12.24.

More characteristics can be extracted in PCS which include the possibility to observe the phonon spectra. In this study we are in the possibility to correlate structure observed with phonon spectrum in the structure obtained

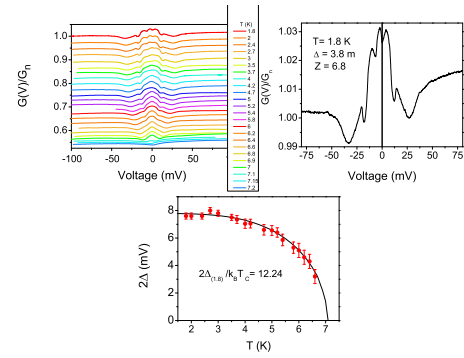


FIG. 4: (Color online) Normalized differential conductance measured from 1.8 to 7.2 K, left panel and right panel shows the spectroscopic features with BTK at 1.8 K, note the additional structure above the energy gap features. Determination of the gap feature gave  $\Delta = 3.8$  meV, and  $Z = 6.8$ , the black continuous line is experimental data. The lower panel displays the evolution with temperature of the gap, extracted of the characteristics. The fitting was performed only from low temperature to 6.8 K. However, extrapolation at high temperature indicates features close to 7.2 K.  $2\Delta/K_B T_C$  ratio value is 12.24.

in our PCS's. Fig. 11 shows the spectra "phonon density of states" obtained in four PCS's once that the second derivative of the voltage respect to the current was calculated,  $d^2V/dI^2 - \text{Bias voltage}-\Delta$ , (this is show in lower inset). The upper panels, we plotted the normalized differential conductance of Pb obtained by tunneling as in Parks book [35], and the phonon density of states of the  $\text{Bi}_2\text{Se}_3$  as given by Rauh [36]. The lower inset displays our results, we noted some similar structure with the real data of the upper inset. There is a correlation between the two spectrum, the obtained here, and the Pb and  $\text{Bi}_2\text{Se}_3$  already known. We believe that further analysis of these spectrum are necessities in order to have a better understanding of the manner the two systems are interacting.

Lastly, in this study we found different transition temperatures with the different junctions studied, the different transition temperatures were because the proximity coupling due to the contact closeness of the two materials. The variations in the  $T_C$  were from 2.7 to 7.1 K. The coupling values for the ratio,  $2\Delta/K_B T_C$ , in distinct PCS, were bigger than for Pb, which is a strong coupled superconductor with the bigger values of all known superconductors. As mentioned the energy gap characteristics were fitted with the BTK model and parameter,  $Z$ . This varies from  $\sim 0.7$  to 7.0. The results show the energy gap evolution with temperature, and follows BCS theory. In addition, extra information was obtained with the study of the second derivative of the voltage respect to the current ( $d^2V/dI^2 - \text{Bias voltage}-\Delta$ ), which provides information related to phonon spectrum. In old studies with normal superconductors is a generalized test of energy



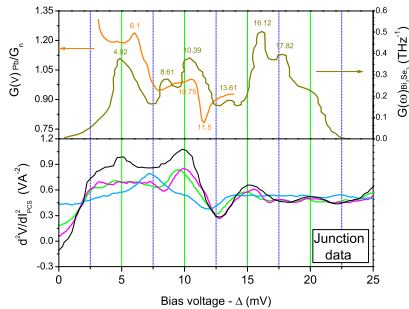


FIG. 5: (Color online) This figure displays the density of states of the phonon structure of Pb in the upper inset (obtained by tunneling measurements (orange line) [35], and the phonon structure of  $\text{Bi}_2\text{Se}_3$  as taken of literature (green line) [36]. Lower inset shows our experimental data, the second derivative of  $dV/dI$  of four junctions with the TI-Pb sample. Qualitatively it seems a close concordance with our data.

of the phonons that couples the superconducting pairs. The background in the early studies performed in tunnel junctions,  $G(V)$ –*Bias voltage* was related to the phonon density interacting to form the superconducting state. In PCS the initial studies related to phonon spectrum was given by I.K. Yanson [32].

The results and characteristics of this new  $\text{Bi}_2\text{Se}_3$ -Pb compound is resumed in our obtained data. Very strong coupled limits by proximity effect induced with Pb were observed. At the moment many questions remain, but it is convenient to mention that because in TI the surface states are symmetry protected, and thus exist particle number conservation and time reversal symmetry, and in addition in 3D the Fermi surface may be in the conduction or valence band because the number of defect in natural material. However this  $\text{Bi}_2\text{Se}_3$  it was suggested that the surface states may be considered as a new type of 2 dimensional electron gas, therefore electronic characteristic for the coupling may be similar to the cuprate superconductors. According this 2-d system has to be related to the so strong coupling limit [3, 4, 23].

In Conclusion; we studied with PCS's the system formed by a thin layers of the  $\text{Bi}_2\text{Se}_3$  single crystal glued to a foil of Pb and pressed to the TI with diluted silver paint. The junctions were formed with  $\text{Bi}_2\text{Se}_3$ -Pb system, the junction was formed with an W(Au) wire as second electrode firmly put on the surface of the TI. Measurements were performed with the normal tools for tunneling or metallic contacts; lock-in amplifier and bridge, an MPMS by Quantum Design used as the cryostat to control the temperature. The characteristics of the junctions were determined at low temperature, 1.7 or 2 K and to 10 K. In all junctions the evolution with temperature of the gap feature follows BCS, with different transition temperatures. The junctions characteristics indicate superconducting proximity effect with different couplings, depending on the closeness with Pb. The energy gap value was determined with BTK model, and with BCS parameter,  $2\Delta/K_B T_C$ , this varies from 10 to 23. The extreme values of the ratio is indicative of an anomalous strong coupling, never observed before. It is important to mention that the anomalous big value of the ratio was observed in all junctions, those values indicate the influence of the coupling strength but not in the transition temperature. This value of the ratio is not clear in the relationship of the electronic coupling strength with the transition temperature; The junction with small  $T_C$  has the biggest ratio, whereas for similar  $T_C$  values the ratio is approximately equal. As mentioned by other researches in Cu- $\text{Bi}_2\text{Se}_3$  similar big values were found and without a clear interpretation of the results [37–40]. We conclude that in this topic more theoretical and experimental work are necessary to understand the new behavior, find correlations in different TI and perform studies with weak and strong coupled superconductors, using PCS junctions with simple superconducting elements as Al, Sn, In.

## ACKNOWLEDGMENTS

We thanks to Prof. R. Cava for kindly provide us the method to growth the single crystals. For grant by DGAPA-UNAM, project IN106014. P. Arevalo-lópez thanks to CONACYT for scholarship number 216073, And also to J. Morales, A. López.

- 
- [1] Y. Xia, D. Qian, D. Hsieh, L. Wray, A. Pal, H. Lin, A. Bansil, D. Grauer, Y. S. Hor, R. J. Cava and M. Z. Hasan, *Nature Phys.* **5**, 398 (2009).
  - [2] Y. L. Chen, J. G. Analytis, J.-H. Chu, Z. K. Liu, S.-K. Mo, X. L. Qi, H. J. Zhang, D. H. Lu, X. Dai, Z. Fang, S. C. Zhang, I. R. Fisher, Z. Hussain and Z. X. Shen, *Science* **325**, 178 (2009).
  - [3] M. Z. Hasan and C. L. Kane, *Rev. Modern Phys.* **82**, 3045 (2010).
  - [4] Xiao-Liang Qi, Shou-Cheng Zhang, *Rev. Moder. Phys.*

- 83**, 747 (2011).
- [5] L. Andrew Wray, Su-Yang Xu, Yuqi Xia, Yew San Hor, Dong Qian, Alexei V. Fedorov, Hsin Lin, Arun Bansil, Robert J. Cava and M. Zahid Hasan, *Nat. Phys.* **6**, 855 (2010).
- [6] M. Kriener, Kouji Segawa, Zhi Ren, Satoshi Sasaki, and Yoichi Ando, *Phys. Rev. Lett.* **106**, 127004 (2011).
- [7] Y. S. Hor, A. J. Williams, J. G. Checkelsky, P. Roushan, J. Seo, Q. Xu, H.W. Zandbergen, A. Yazdani, N. P. Ong, and R. J. Cava, *Superconductivity in  $\text{Cu}_x\text{Bi}_2\text{Se}_3$  and its*

- Implications for Pairing in the Undoped Topological Insulator* Phys. Rev. Lett. 104, 057001 (2010).
- [8] Y.S. Hor, J.G. Checkelsky, D. Qu, N.P. Ong, R.J. Cava, *Superconductivity and non-metallicity induced by doping the topological insulators  $\text{Bi}_2\text{Se}_3$  and  $\text{Bi}_2\text{Te}_3$*  Phys. Chem. Solids, 572 - 576 (2011).
- [9] Timothy H. Hsieh and Liang Fu, *Majorana Fermions and Exotic Surface Andreev Bound States in Topological Superconductors: Application to  $\text{Cu}_x\text{Bi}_2\text{Se}_3$*  Phys. Rev. Lett. 108, 107005 (2012).
- [10] Satoshi Sasaki, M. Kriener, Kouji Segawa, Keiji Yada, Yukio Tanaka, Masatoshi Sato, and Yoichi Ando, *Topological Superconductivity in  $\text{Cu}_x\text{Bi}_2\text{Se}_3$*  Phys. Rev. Lett. 107, 217001 (2011).
- [11] Parisa Zareapour, Alex Hayat, Shu Yang F. Zhao, Michael Kreshchuk, Achint Jain, Daniel C. Kwok, Nara Lee, Sang-Wook Cheong, Zhijun Xu, Alina Yang, G.D. Gu, Shuang Jia, Robert J. Cava and Kenneth S. Burch *Proximity-induced high-temperature superconductivity in the topological insulators  $\text{Bi}_2\text{Se}_3$  and  $\text{Bi}_2\text{Te}_3$*  Nat Commun 3, 1056 (2012).
- [12] G. Koren, T. Kirzhner, E. Lahoud, K. B. Chashka, and A. Kanigel, *Proximity-induced superconductivity in topological  $\text{Bi}_2\text{Te}_2\text{Se}$  and  $\text{Bi}_2\text{Se}_3$  films: Robust zero-energy bound state possibly due to Majorana fermions* Phys. Rev. B 84, 224521 (2011).
- [13] Mei-Xiao Wang, Canhua Liu, Jin-Peng Xu, Fang Yang, Lin Miao, Meng-Yu Yao, C. L. Gao, Chenyi Shen, Xucun Ma, X. Chen, Zhu-An Xu, Ying Liu, Shou-Cheng Zhang, Dong Qian, Jin-Feng Jia, Qi-Kun Xue, *The Coexistence of Superconductivity and Topological Order in the  $\text{Bi}_2\text{Se}_3$  Thin Films* Science 336, 52 (2012).
- [14] Desheng Kong, Wenhui Dang, Judy J. Cha, Hui Li, Stefan Meister, Hailin Peng, Zhongfan Liu, and Yi Cui, *Few-Layer Nanoplates of  $\text{Bi}_2\text{Se}_3$  and  $\text{Bi}_2\text{Te}_3$  with Highly Tunable Chemical Potential*, Nano Lett. 10, 2245 - 2250 (2010).
- [15] Tetsuroh Shirasawa, Masato Sugiki, Toru Hirahara, Masaki Aitani, Terufusa Shirai, Shuji Hasegawa, and Toshio Takahashi, *Structure and transport properties of  $\text{Cu}$ -doped  $\text{Bi}_2\text{Se}_3$  films*, Phys. Rev. B 89, 195311 (2014).
- [16] Charles. P. Poole Jr., Handbook of superconductivity. Academic Press (2000).
- [17] D. Daghero, M. Tortello, G. A. Ummarino and R. S. Gonnelli, *Directional point-contact Andreev-reflection spectroscopy of Fe-based superconductors: Fermi surface topology, gap symmetry, and electronboson interaction*, Rep. Prog. Phys. 74 (2011).
- [18] Z. Schlesinger, R. T. Collins, F. Holtzberg, C. Feild, and S. H. Blanton, *Superconducting Energy Gap and Normal-State Conductivity of a Single-Domain  $\text{YBa}_2\text{Cu}_3\text{O}_7$  Crystal*, Phys. Rev. Lett. 65, 801 (1990).
- [19] A. Dubroka, K. W. Kim, M. Rössle, V. K. Malik, A. J. Drew, R. H. Liu, G. Wu, X. H. Chen, and C. Bernhard, *Superconducting Energy Gap and c-Axis Plasma Frequency of  $(\text{Nd},\text{Sm})\text{FeAsO}_{0.82}\text{F}_{0.18}$  Superconductors from Infrared Ellipsometry* Phys. Rev. Lett. 101, 097011 (2008).
- [20] R. Manzke, T. Buslaps, R. Claessen and J. Fink, *On the Superconducting Energy Gap in  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{0.8}$  Investigated by High-Resolution Angle-Resolved Photoemission*, Europhysics Lett. 9, 477 (1989).
- [21] Mark Lee, D. B. Mitzi, A. Kapitulnik, and M. R. Beasley, *Electron tunneling and the energy gap in  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_x$*  Phys. Rev. B 39, 801 (1989).
- [22] R. Escudero, Rodolfo E. Lopez-Romero, *The energy gap of the compound  $\text{FeSe}_{0.5}\text{Te}_{0.5}$  determined by specific heat and Point Contact Spectroscopy*, Solid state Comm. 220, 2124 (2015).
- [23] Liang Fu and C. L. Kane, *Superconducting Proximity Effect and Majorana Fermions at the Surface of a Topological Insulator*, Phys. Rev. Lett. 100 (2008).
- [24] G.E. Blonder, M. Tinkham, and T. M. Klapwijk, *Transition from metallic to tunneling regimes in superconducting microconstrictions: Excess current, charge imbalance, and supercurrent conversion*, Phys. Rev. B, 25 (1982).
- [25] Haijun Zhang, Chao-Xing Liu, Xiao-Liang Qi, Xi Dai, Zhong Fang and Shou-Cheng Zhang, *Topological insulators in  $\text{Bi}_2\text{Se}_3$ ,  $\text{Bi}_2\text{Te}_3$  and  $\text{Sb}_2\text{Te}_3$  with a single Dirac cone on the surface* Nat. Phys. 5, 438 (2009).
- [26] D. Hsieh, Y. Xia, D. Qian, L. Wray, J. H. Dil, F. Meier, J. Osterwalder, L. Patthey, J. G. Checkelsky, N. P. Ong, A. V. Fedorov, H. Lin, A. Bansil, D. Grauer, Y. S. Hor, R. J. Cava and M. Z. Hasan, *A tunable topological insulator in the spin helical Dirac transport regime* Nature 460, 1101 (2009).
- [27] J. R. Wiese and L. Muldrew, *Lattice constants of  $\text{Bi}_2\text{Se}_3$ - $\text{Bi}_2\text{Te}_3$  solid solution alloys* J. Phys. Chem. Solids 15, 13 (1960).
- [28] Guanhua Zhang, Huajun Qin, Jing Teng, Jiandong Guo, Qinlin Guo, Xi Dai, Zhong Fang, and Kehui Wua, *Quintuple-layer epitaxy of thin films of topological insulator  $\text{Bi}_2\text{Se}_3$* , Appl. Phys. Lett. 95, 053114 (2009).
- [29] Duming Zhang, Jian Wang, Ashley M. DaSilva, Joon Sue Lee, Humberto R. Gutierrez, Moses H. W. Chan, Jainendra Jain, and Nitin Samarth, *Superconducting proximity effect and possible evidence for Pearl vortices in a candidate topological insulator* Phys. Rev. B 84, 165120 (2011).
- [30] Fan Yang, Fanming Qu, Jie Shen, Yue Ding, Jun Chen, Zhongqing Ji, Guangtong Liu, Jie Fan, Changli Yang, Liang Fu, and Li Lu, *Proximity-effect-induced superconducting phase in the topological insulator  $\text{Bi}_2\text{Se}_3$*  Phys. Rev. B 86, 134504 (2012).
- [31] Gad Koren, Tal Kirzhner, Yoav Kalcheim and Oded Millo, *Signature of proximity-induced  $p_x + ip_y$  triplet pairing in the doped topological insulator  $\text{Bi}_2\text{Se}_3$  by the s-wave superconductor  $\text{NbN}$* , EPL, 103, 67010 (2013).
- [32] I.K. Yanson, *Nonlinear effects in the electric conductivity of point junctions and electron-phonon interaction in normal metals*, Sov. Phys. JETP 39, 506 (1974).
- [33] R. Escudero, R. E. Lopez-Romero, and F. Morales, *Study of the hidden-order of  $\text{URu}_2\text{Si}_2$  by point contact tunnel junctions*, J. Phys.:Condens.Matter 27, 015701 (2015).
- [34] U. Fano, *Effects of Configuration Interaction on Intensities and Phase Shifts*, Phys. Rev., 124, 1866 (1961).
- [35] R. D. Parks, *Superconductivity*, Marcel Dekker, 1, 597 (1969).
- [36] H Rauh, R Geick, H Kohler, N Nucker and N Lehner, *Generalized phonon density of states of the layer compounds  $\text{Bi}_2\text{Se}_3$ ,  $\text{Bi}_2\text{Te}_3$ ,  $\text{Sb}_2\text{Te}_3$  and  $\text{Bi}_2(\text{Te}_{0.5}\text{Se}_{0.5})_3$ ,  $(\text{Bi}_{0.5}\text{Sb}_{0.5})_2\text{Te}_3$*  J. Phys. C: Solid State Phys., 14, 2705-2712 (1981).
- [37] T. Kirzhner, E. Lahoud, K. B. Chaska, Z. Salman, and A. Kanigel, *Point-contact spectroscopy of  $\text{Cu}_{0.2}\text{Bi}_2\text{Se}_3$  single crystals* Phys. Rev. B 86, 064517 (2012).
- [38] X. Chen, C. Huan, Y. S. Hor, C. A. R. Sá de Melo, and Z. Jiang, *Point-contact Andreev reflection spectroscopy*

- of candidate topological superconductor  $\text{Cu}_{0.25}\text{Bi}_2\text{Se}_3$ , arXiv: 1210.6054v1. 22Oct (2012).
- [39] Niv Levy, Tong Zhang, Jeonghoon Ha, Fred Sharifi, A. Alec Talin, Young Kuk, and Joseph A. Stroscio, *Experimental Evidence for s-Wave Pairing Symmetry in Superconducting  $\text{Cu}_x\text{Bi}_2\text{Se}_3$  Single Crystals Using a Scanning Tunneling Microscope*, Phys. Rev. Lett. 110, 117001 (2013).
- [40] Ai Yamakage, Keiji Yada, Masatoshi Sato, and Yukio Tanaka, *Theory of tunneling conductance and surface-state transition in superconducting topological insulators*, Phys. Rev. B 85, 180509 (2012).